

HEAT INSULATION MATERIALS

UDC 666.9-405.8

STRUCTURE FORMATION OF CELLULAR HEAT-INSULATION MATERIAL FROM COLD-SOLIDIFYING LIQUID-GLASS COMPOSITION

V. V. Samoilenko¹ and V. V. Firsov^{1,2}

Translated from *Steklo i Keramika*, No. 8, pp. 14–16, August, 2011.

The possibility of obtaining foamed heat-insulation material at room temperature on the basis of liquid glass with calcium-containing additives is examined. A method of controlling gas generation and solidification of a liquid-glass composition by changing the silicate modulus of liquid glass is shown.

Key words: cellular articles, liquid glass, silicate modulus, setting time, heat-insulation materials.

The most effective heat-insulation material is still foam glass — a rigid, high-porosity, heat-insulation material with a closed cellular structure, which consists of solidified glass foam with 0.5–3 mm cells. However, despite a number of advantages, the complicated and energy-intensive technology needed to produce it and, correspondingly, the high cost of the final product make it impossible to organize wide production of block foam glass [1–4].

A number of publications on this subject have appeared in the last few years, and research on developing heat-insulation materials with properties similar to those of foam glass is ongoing. Most technologies which have been proposed are based on the same principles — heating a high-dispersion mix to the temperature of the transition into the plastic state ($> 700^{\circ}\text{C}$), foaming by gases released during heating, and prolonged firing, which is why the production process is highly energy intensive. [5–7].

An alternative to foam glass — heat-insulation material based on liquid glass — can be obtained with much lower energy consumption. This material possesses a quite rigid cellular structure, low density, and low thermal conductivity and it is inflammable, biostable, and environmentally friendly. Its drawbacks are quite high water absorption and low stability in water, which can be eliminated by heat-treating articles at 300–400°C [8, 9].

To transfer the liquid glass into the solid state the water must be removed or the liquid glass must be treated chemi-

cally using solidifying agents or both actions must be taken simultaneously. The processes occurring during solidification of the liquid-glass compositions are quite complex and have been under study for many years.

One of the basic and important characteristics of liquid glass is the silicate modulus — the ratio $\text{SiO}_2/\text{M}_2\text{O}$ (where M is K, Na, or Li), which for commercial products lies in the interval 2–4. The silicate modulus itself determines the chemical properties of liquid glass [9, 10]. A large number of research results, patents, and inventor's certificates give prescriptions for compositions using liquid glass with a fixed modulus, but as a rule its effect on the solidification processes and properties are not studied.

It is known that a concentrated solution of sodium silicate with modulus 1–2 consists primarily of hydrated cations of alkali metal and monomeric silicon-oxygen anions, which are in dynamic equilibrium with monomeric silica $\text{Si}(\text{OH})_4$. As the modulus increases, polymeric silicate ions as well as colloidal spherical particles form in solution; these particles and ions become nuclei for a subsequent process where at higher modulus even larger colloidal-ionic varieties form. Such a complex composition, formally characterized by the silicate modulus, makes an imprint on the physical and chemical properties of alkali silicates. Transformations which are characteristic for colloidal chemistry (gel formation, coagulation, and others) and accompany the main chemical transformations inhere in them to a large degree [9, 10].

Solutions of alkali silicates react with solid substances which contain alkali-earth metals — various clays, glass, sols, and slags as well as compounds of these metals such as

¹ Institution of the Russian Academy of Sciences — Institute of Chemical-Energy Technologies, Siberian Branch of the Russian Academy of Sciences, Biisk, Altai Krai, Russia.

² E-mail: labmineral@mail.ru.

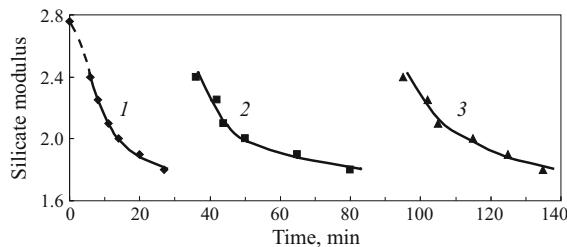


Fig. 1. Solidification time of a composition versus the silicate modulus of liquid glass: 1) flowability loss; 2, 3) setting onset and completion, respectively.

carbonates, sulfates, phosphates, fluorides, silicates, oxides, and hydroxides. The solidification time can vary from zero to infinity. It depends strongly on the type of solid material, its crystal structure or degree of amorphousness, particle size, temperature, as well as on the concentration and liquid-glass modulus [10, 11].

In the present work attempts are made to determine the influence of the modulus on the solidification kinetics and the possibility of controlling the process in order to obtain porous materials with prescribed properties.

Liquid glass with silicate modulus 2.7–3.5 interacts very actively with water-soluble calcium-containing reagents. Experiments have shown that with gypsum, cement, and lime solidification occurs even as the components are being mixed, and it is impossible to obtain a homogeneous composition. A technologically more efficient composition is one based on calcium hydroxide (ground air-slaked lime) to which chalk is added. Lime dissolves quite rapidly in liquid glass, permits effective solidification of liquid-glass mixtures, and makes it possible to regulate the setting time over a wide range. Chalk does not dissolve in liquid glass at the usual temperature; on the one hand it has been used as a filler and viscosity regulator and on the other hand as a solidifying agent capable of interacting chemically with silicates at elevated temperatures, thereby increasing the stability of the material in water.

The samples were prepared according to the following prescription (mass parts): sodium liquid glass with density 1.43 g/cm³ — 10; fine technical-grade chalk — 3; air-slaked lime — 2. The silicate modulus of liquid glass was changed by dissolving a computed amount of sodium hydroxide in it.

Figure 1 displays the kinetic curves of solidification at room temperature for compositions based on liquid glass with different silicate modulus.

Setting onset and completion times were determined following GOST 310.1–76 on a Vick apparatus by inserting 1.1 mm in diameter needles into the mix under a fixed load (300 g) produced by the moving part of the apparatus. Setting onset is defined as the time from mixing of the mix to the moment when in 30 sec the needle does not reach a distance 2–4 mm from the bottom of a 40 mm high sample. The completion of setting is the time when the needle enters into the mix to no more than 1–2 mm.

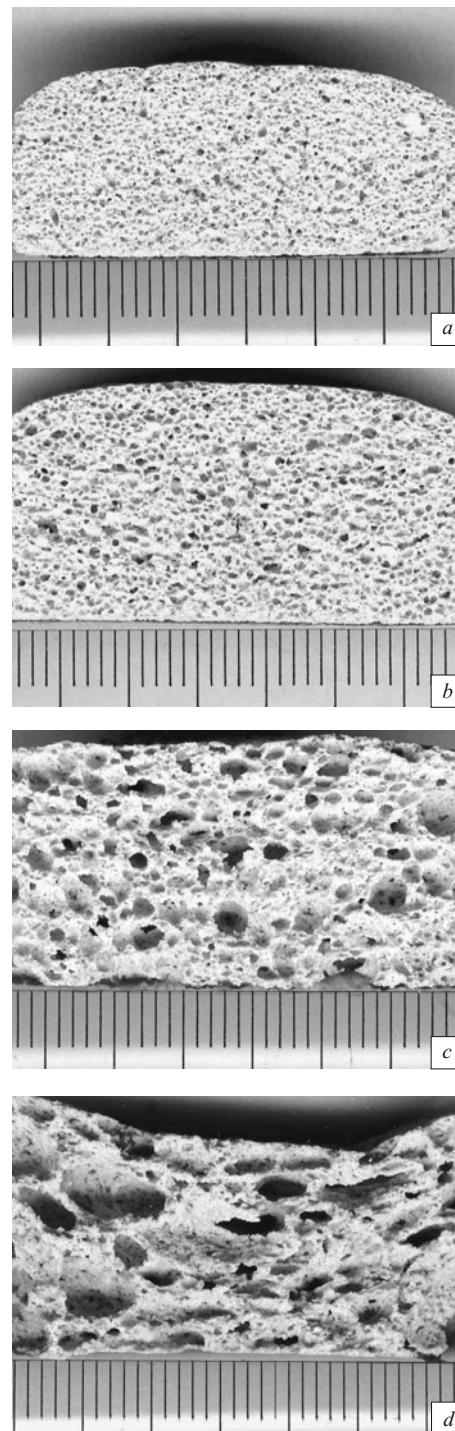


Fig. 2. Samples of cellular material obtained from compositions based on liquid glass with silicate modulus 2.40 (a), 2.25 (b), 2.10 (c), and 2.00 (d).

Aside from this, the flowability loss time, defined as the time when the mix can no longer be drawn by a small glass rod touching it, was measured.

To produce porosity aluminum powder was introduced as a gas generating agent into the composition; aluminum powder is widely used to produce foam concrete. The essence

of the gas-generation process is the interaction between aluminum and the alkali component. This interaction is accompanied by the release of hydrogen gas, which results in the formation of pores in the material. The kinetics of gas release must conform to the rate of growth of the viscosity and is completed by the time the composition loses its mobility.

According to Fig. 1, as the silicate modulus decreases and, correspondingly, the basicity pH increases, the solidification time of the samples increases in a regular manner. Therefore, it should be possible to adjust the solidification parameters.

On the other hand, it is known that for otherwise equal conditions, the kinetics of gas generation strongly depends on the basicity of the medium. Thus, for all practical purposes, liquid glass with modulus 2.7 and higher does not interact with aluminum, since an inert silica-gel film forms on its surface. Lowering the silicate modulus of the liquid-glass composition increases the number of free hydroxyl groups capable of reacting with metal and simultaneously impeding coagulation of the silica. If for liquid-glass modulus greater than 2.7 the composition solidifies rapidly but virtually no gas is generated, then by lowering the modulus to 1.8 – 2.4 conditions under which these two processes occur in an optimal manner can be found.

Figure 2 shows samples of cellular material obtained from compositions containing liquid glass with different moduli.

The sample with modulus 2.25 (see Fig. 2b) has the best structure. In this structure, 0.5 – 1.00 mm pores are distributed uniformly. The modulus of the next sample is 2.1 (Fig. 2c); this sample possesses the lowest density. However, its structure is characterized by quite large pores, indicating the onset of bubble coalescence. For the sample with modulus 2.4 (Fig. 2a) gas generation proceeds much more slowly than solidification; for the sample with modulus 2 (Fig. 2d) the solidification time is too long, the gas generation process is fast, and there is enough time for bubbles to combine and migrate to the outside.

In summary, these investigations have shown that by purposefully changing only a single basic characteristic of

liquid glass — the silicate modulus — it is possible to control the kinetics of solidification as well as the rate of gas generation in order to produce a cellular structure of the material at room temperature.

REFERENCES

1. I. I. Kitaigorodskii, *The Technology of Glass* [in Russian], Gosstroizdat, Moscow (1961).
2. F. Shill, *Foam Glass* [in Russian], Stroizdat, Moscow (1965).
3. V. A. Kitaitsev, *The Technology of Heat-Insulation Materials* [in Russian], Stroizdat, Moscow (1970).
4. B. K. Demidovich, *Foam Glass* [in Russian], Nauka i Tekhnika, Minsk (1975).
5. V. I. Vereshchagin and S. N. Sokolova, "Granular foam glass-crystalline heat-insulation material from zeolite-containing rock," *Stoit. Mater.*, No. 3, 66 – 67 (2007).
6. O. V. Kaz'mina, V. I. Vereshchagin, and A. I. Abiyaka, "Prospects for using fine quartz sands in the production of foam glass-crystalline materials," *Steklo Keram.*, No. 9, 28 – 30 (2008); O. V. Kaz'mina, V. I. Vereshchagin, and A. I. Abiyaka, "Prospects for use of finely disperse quartz sands in production of foam-glass crystalline materials," *Glass Ceram.*, **65**(9 – 10), 319 – 321 (2008).
7. O. V. Kaz'mina, "Effect of the component composition and redox properties of mixes on foaming of pyroplastic silicate pastes," *Steklo Keram.*, No. 4, 13 – 17 (2010); O. V. Kaz'mina, "Effect of the component composition and oxidation – reduction characteristics of mixes on foaming of pyroplastic silicate pastes," *Glass Ceram.*, **67**(3 – 4), 109 – 113 (2010).
8. V. A. Lotov and V. A. Kutugin, "Thermo-foam-silicate articles based on liquid-glass compositions," *Steklo Keram.*, No. 1, 6 – 10 (2008); V. A. Lotov and V. A. Kutugin, "Formation of a porous structure of foam silicates based on liquid-glass compositions," *Glass Ceram.*, **65**(1 – 2), 6 – 10 (2008).
9. V. I. Kornev and V. V. Danilov, *Soluble and Liquid Glass* [in Russian], Stroizdat, St. Petersburg (1996).
10. M. M. Sychev, *Inorganic Glues* [in Russian], Khimiya, Leningrad (1974).
11. P. A. Borsuk and A. M. Lyass, *Liquid Self-Hardening Mixtures* [in Russian], Mashinostroenie, Moscow (1979).
12. *GOST 310.1-76. Cements. Methods for Determining Normal Consistency, Setting Times, and Uniformity of Volume Measurements* [in Russian], Reprint (November 1992) with amendment No. 1, approved August 1984 (IUS 1-85), Moscow (1992).